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(71)Applicant : TOSOH CORP

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(72)Inventor : KAGAWA TAKUMI  
SAKKA HIDEO

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## (54) BROMINATED STYRENE OLIGOMER, ITS PRODUCTION AND FLAME-RETARDANT RESIN COMPOSITION COMPOUNDED WITH THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject oligomer readily meltable and dispersible into resins such as a general-purpose polypropylene and an impact-resistant polystyrene, capable of developing high flame-retardance, heat resistance and processability without lowering mechanical properties of resin and without changing the color of resin, by possessing specific physical properties.

SOLUTION: This oligomer shows physical properties of 300-1,200 weight- average molecular weight calculated as polystyrene, 40-70 wt.% of bromine content, 50-150°C softening point as light yellow powder, heat stability measured by a thermobalance of 5% reduction at  $\geq 300^{\circ}\text{C}$  and 50% reduction at  $\geq 350^{\circ}\text{C}$ . The oligomer is produced by brominating a styrene oligomer having 300-1,200 weight-average molecular weight obtained by cationic polymerization with a brominating agent such as bromine chloride in a solvent such as dichloromethane inert to the reaction in the presence of a catalyst such as antimony trichloride. The oligomer is meltable and dispersible into an acrylonitrile-styrene-butadiene copolymer resin, a polybutylene terephthalate, etc.

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## CLAIMS

## [Claim(s)]

[Claim 1] For 300 degrees C or more and 50% reduction, 5% reduction is [ the thermal stability in the range of 300-1200 the weight average molecular weight of polystyrene conversion is the powder of 40 - 70 % of the weight of bromine contents, and the light yellow of the range of 50-150 degrees C of softening temperatures, and according to thermobalance measurement ] the bromination styrene oligomer to which it is characterized by showing physical properties 350 degrees C or more.

[Claim 2] The manufacture approach of bromination styrene oligomer according to claim 1 that the weight average molecular weight obtained by cationic polymerization carries out the description of brominating the styrene oligomer of the range of 300-1200 by the bromination agent under catalyst existence.

[Claim 3] The flame-retardant-resin constituent which comes to blend bromination styrene oligomer according to claim 1 with resin.

[Claim 4] The flame-retardant-resin constituent according to claim 3 characterized by carrying out 5-50 weight section combination of the bromination styrene oligomer according to claim 1 to the resin 100 weight section.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the bromination styrene oligomer which is excellent in new quality, its manufacture approach, and the flame-retardant-resin constituent which comes to blend it. The bromination styrene oligomer of this invention is a compound useful to flameproofing of synthetic resin, and it is possible to use for flameproofing of the resin used abundantly at various electric products etc.

#### [0002]

[Description of the Prior Art] About flameproofing of synthetic resin, to various resin, various bromine system flame retarders, a phosphoric ester system flame retarder, and an inorganic flame retardant are used, and proper use is made by the application. As a typical flame retarder, deca BUROMO diphenyloxide, tetrabromobisphenol A, TBA-epoxy oligomer, bromination polystyrene, triphenyl phosphate, a magnesium hydroxide, an aluminum hydroxide, etc. are mentioned.

[0003] Moreover, as a bromine system flame retarder which has a styrene unit, the bromination styrene oligomer of about 1400 is marketed for the polystyrene equivalent weight mean molecular weight other than the above-mentioned bromination polystyrene.

#### [0004]

[Problem(s) to be Solved by the Invention] Conventional bromination polystyrene has the problem which causes the sharp fall of combination resin physical properties, when it blends with general-purpose resin, such as high-impact-polystyrene (it omits Following HIPS) and AKURORONI tolyl-styrene-butadiene copolymerization resin (following ABS \*\*\*\*) and a polo propylene (it omits Following PP), since weight average molecular weight is as high as about 200,000 although used for the engineering plastics mainly represented by nylon, polyethylene terephthalate, and polybutylene terephthalate.

[0005] On the other hand, although commercial styrene oligomer is applicable to general-purpose resin, such as the above, HIPS, and ABS, PP, thermal resistance is bad and there is a problem which the color tone of combination resin presents brown.

#### [0006]

[Means for Solving the Problem] It came to complete a header and this invention for the bromination styrene oligomer which this invention persons use as a raw material the styrene oligomer obtained by cationic polymerization as a result of examining the bromination styrene oligomer of high quality wholeheartedly, and is obtained by brominating showing the combination resin physical properties which were conventionally superior to elegance by excelling in thermal resistance and setting weight average molecular weight of a raw material to 200-1000.

[0007] That is, the range of the weight average molecular weight of heavy polystyrene conversion is 300-1200, this invention is the powder of 40 - 70 % of the weight of bromine contents, and the light yellow of the range of 50-150 degrees C of softening temperatures, and the thermal stability by thermobalance measurement is a flame-retardant-resin constituent with which 5% reduction comes to blend 300 degrees C or more, the bromination styrene oligomer characterized by 50% reduction showing physical properties 350 degrees C or more, its manufacture approach, and it.

[0008] Hereafter, this invention is explained to a detail.

[0009] The range of the weight average molecular weight of heavy polystyrene conversion is 300-1200, the bromination styrene oligomer of this invention is the powder of 40 - 70 % of the weight of bromine contents, and the light yellow of the range of 50-150 degrees C of softening temperatures, and, as for the thermal stability by thermobalance measurement, 300 degrees C or more and 50% reduction show [ reduction ] physical properties 350 degrees C or more 5%.

[0010] The styrene oligomer of the raw material possessed to this invention is the oligomer obtained by making a styrene monomer react among a solvent inactive for a reaction under cationic polymerization catalyst existence, such as an aluminum chloride, 3 ferric chloride, an antimony trichloride, and trifluoro borane etherate, and the thing of 300-1200 can apply [ weight average molecular weight ] it to this invention.

[0011] The bromination styrene oligomer of this invention can be obtained by making the styrene oligomer and the bromination agent of a raw material react among a solvent inactive for a reaction, and under catalyst existence.

[0012] as a catalyst applicable to this invention -- concrete -- an aluminum chloride, the aluminium bromide, a ferric chloride, and bromination -- these catalysts are chosen with the second iron, a titanium tetrachloride, a titanium trichloride, an antimony pentachloride, an antimony trichloride, and the number of nuclear bromination that Lewis acid catalysts, such as antimony, tin chloride, and trifluoro borane ETERATO, are mentioned 3 bromination, and is made into the purpose. moreover, these catalysts are independent -- or even if two or more sorts use it, mixing, it is convenient in any way.

[0013] the unit styrene unit of the raw material oligomer possessed for a reaction as an amount of catalysts -- receiving -- all amounts -- usable -- concrete -- 0.01-mol [/mol] % -- 100-mol [/mol] % from a ratio -- it is the range of a ratio. Use little also to remainder has a slow reaction, or it may deactivate with the impurity originating in a raw material and a solvent, and, on the other hand, use superfluous to remainder is not economical. Therefore, it is the range of 0.1-mol [/mol] % - 40-mol [/mol] % preferably.

[0014] or [ using properly according to the number of nuclear bromination which are specifically a bromine and a bromine chloride and is made into the purpose as a bromination agent applicable to this invention, the catalyst to be used, and the target quality of the specified substance acquired ] -- or it is mixed and used. In addition, when using a bromine chloride, chlorination occurs as side reaction, and after about 0.1 - 5% of the weight of chlorine has joined together on a ring in the specified substance, it contains. Moreover, in order to obtain the white specified substance more, it is desirable to use a bromine chloride.

[0015] As amount of the bromination agent used, it changes with the number of nuclear bromination of the unit unit of the raw material oligomer made into the purpose. Usually, although below the amount of 5-mol double is used more than the amount of equimolar double to the target number of nuclear bromination, preferably, it is the range below the amount of 1.5-mol double more than this amount of mol double, and the amount used is decided by the class of catalyst to be used, and the reaction condition.

[0016] As a solvent used for a reaction, to a bromination agent and a catalyst, if inactive, all things will be usable and, specifically, dichloromethane, dibromomethane, chloroform, bromoform, a carbon tetrachloride, 1,2-dichloroethane, 1,1,2-trichloroethane, etc. will be mentioned.

[0017] Although it is usable at all quantitative ratios, since the reaction mixture viscosity after reaction termination becomes high below in the amount of 1 weight double as amount of the solvent used to the raw material oligomer possessed for a reaction, it is not desirable, and above the amount of 100 weight double, it is not economical. Therefore, it is the range of the amount of 80 weight double more than the amount of 1.2 weight double preferably.

[0018] Although it changes as reaction temperature with whenever [ nuclear bromination / which is made into a bromination agent, a catalyst, and the purpose ] Usually, this reaction of the drop time of the bromination agent carried out in -30 degrees C - 20 degrees C when using a bromine and using the range of 0 degree C - 60 degrees C and a bromine chloride, or when using a bromine and a bromine chloride together is exothermic reaction. in addition -- in order [ and ] to accompany hydrogen halide gas by generating -- control of reaction temperature -- possible -- in addition -- and if it is under the condition which the occurring hydrogen halide gas can catch out of a system, there will be especially no convention.

[0019] After addition termination of a bromination agent, after treatment may be performed immediately and aging may be performed at predetermined temperature for 1 to 8 hours.

[0020] An excessive bromination agent is eliminated by adding reducing agents, such as a hydrazine and a sodium hydrogensulfite, after reaction termination, subsequently to poor solvents, such as rinsing, a methanol, or hot water, crystallization is carried out by adding and the bromination styrene oligomer of the specified substance is obtained by filtering and drying further.

[0021] The bromination styrene oligomer of this invention demonstrates the fire-resistant high engine performance and combination resin physical properties, without reducing the machine engine performance and color tone of the resin concerned by blending with thermosetting resin or thermoplastics.

[0022] As resin which can blend the bromination styrene oligomer of this invention Specifically For example, phenol resin, a urea resin, melamine resin, an unsaturated polyester resin, Thermosetting resin, such as polyurethane, alkyd resin, and an epoxy resin, and low density polyethylene and ethylene-vinyl acetate

copolymer, polystyrene, High impact polystyrene, form polystyrene, an AKURORINI tolyl-styrene copolymer, An AKURORONI tolyl-styrene-butadiene copolymer (it omits Following ABS), Polypropylene, petroleum resin, polymethylmethacrylate, a polyamide, A polycarbonate, polyethylene terephthalate, polybutylene terephthalate, Thermoplastics, such as polyphenylene ether, is mentioned and the polymer alloy represented by poly car baud NETO-ABS which mixed two or more sorts of thermoplastics, polyphenylene ether-polystyrene, etc. can be illustrated further. Among these A low-density-polyethylene, high-density-polyethylene, and ethylene-vinyl acetate copolymer, Polystyrene, high impact polystyrene, form polystyrene, an AKURORINI tolyl-styrene copolymer, An AKURORONI tolyl-styrene-butadiene copolymer (ABS), polypropylene, Petroleum resin, polymethylmethacrylate, a polyamide, a polycarbonate, Thermoplastics, such as polyethylene terephthalate, polybutylene terephthalate, and polyphenylene ether, The polymer alloy represented by poly car baud NETO-ABS which furthermore mixed two or more sorts of thermoplastics, polyphenylene ether-polystyrene, etc. is suitable resin.

[0023] Although it changes with fire-resistant engine performance made into the class and the purpose of the resin to blend as loadings to the resin of the bromination styrene oligomer of this invention and does not limit especially, 5-50 weight section combination is usually carried out to the resin 100 weight section.

[0024] In blending the bromination styrene oligomer of this invention with resin, fire-resistant assistants, such as an antimony trioxide and sodium antimonate, may be added, and 5-80 weight section addition is usually carried out to the bromination styrene oligomer 100 weight section of this invention in this case. Furthermore, if needed, the light stabilizer of the ultraviolet ray absorbent of a benzotriazol system, 2, 2 and 6, and 6-tetramethylpiperidine derivative, the antioxidant of a hindered phenol system, etc. may be added, and 0.05-5 weight section addition is usually carried out to the flame-retardant-resin constituent 100 weight section of this invention in this case. Inorganic bulking agents, such as an antistatic agent, and talc, glass fiber, may be added if needed besides these.

[0025] As the combination approach to the resin of the bromination styrene oligomer of this invention, when blending with thermosetting resin, when [ which is blended with thermoplastics ] a resin raw material is made to distribute the bromination styrene oligomer derivative of this invention beforehand, a required combination agent may be mixed using a conical blender or a tumbler mixer, and you may pelletize using a twin screw extruder etc. that what is necessary is just to carry out postcure, for example. Especially the processing approach of the flame-retardant-resin constituent obtained by these approaches is not limited, and can perform extrusion molding, injection molding, etc., for example, can obtain the target cast.

[0026]

[Effect of the Invention] Since softening temperature is 200 degrees C or less, the bromination styrene oligomer of this invention discovers the high fire retardancy engine performance and high workability, without carrying out melting distribution and reducing the machine physical properties of resin to resin, such as general-purpose polypropylene, high-impact-polystyrene, and acrylonitrile-styrene-butadiene copolymerization resin, polybutylene terephthalate, a polyamide, polyethylene terephthalate, and a polycarbonate. Moreover, compared with conventional bromination styrene oligomer, it excelled in thermal resistance, and at the time of molding processing, the problem of resin discoloration was lost and application for the coloring application of combination resin also became possible.

[0027]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited only to these examples.

[0028] To the bottom omission of 20l. 5 opening circular separable flask equipped with example 1 agitator and the dropping funnel with a cooling jacket, the weight average molecular weight obtained by cationic polymerization taught styrene oligomer 700g [ of 900 ], 55.0g [ of antimony trichlorides ], and dichloromethane 8000g, and cooled on the ice bath at 0 degree C.

[0029] Subsequently, the dichloromethane solution of the bromine chloride prepared from 1700g [ of bromines ], 690g [ of chlorine ], and dichloromethane 3500g was taught to the dropping funnel with a cooling jacket in 4 steps at 0 degree C, and aging was performed to dropping and a pan at this temperature over 6 hours for 6 hours.

[0030] 1l. of hydrazine water solutions was added 20% of the weight to reaction mixture after reaction termination, and liquids were washed and separated 3 times with 5l. water after eliminating an excessive bromine chloride. After carrying out crystallization of the obtained reaction mixture by dividing into 4 times and adding to 6l. (a total of 24l.) of agitated methanols, when filtration and 1mmHg dried for bottom 120-degree-C of reduced pressure x 4 hours, it obtained the bromination styrene oligomer 1990g light yellow powder made into the purpose.

[0031] The result of the elemental analysis of the obtained bromination styrene oligomer, softening temperature, a nuclear-magnetic-resonance spectrum, an infrared absorption spectrum, a gel permeation chromatograph, and thermobalance measurement is shown.

[0032]

An elemental-analysis result C H Br Cl Measured value 30.6 (% of the weight) 1.5 67.5 0.4 softening temperature: -- 97-129-degree-C nuclear-magnetic-resonance spectrum (CDCl<sub>3</sub>, ppm): -- delta -- 1.0-1.8 (m, 2H), 2.2-2.7 (bs, 1.0H), and 6.5-7.8 (m, 2.3H)

Gel-permeation chromatograph (THF): MW=1038, MN=308, MW/MN=3.37 thermobalance (10-degree-C / min): 5% reduction (325 degrees C), 10% reduction (344 degrees C), 50% reduction (382 degrees C), 90% reduction (515 degrees C).

[0033] Except having changed into the raw material with which weight average molecular weight was obtained by the cationic polymerization of 570 using the same reactor as example 2 example 1, the same actuation as an example 1 was performed and 1760g of powder of bromination styrene oligomer was obtained. An analysis result is shown below like an example 1.

[0034]

An elemental-analysis result C H Br Cl Measured value 30.8 (% of the weight) 1.3 67.0 0.7 softening temperature: -- 78-112-degree-C nuclear-magnetic-resonance spectrum (CDCl<sub>3</sub>, ppm): -- delta 1.0-1.8 (m, 2H) and 2.2-2.7 (bs, 1.0H) and 6.5-7.8 (m, 2.4H)

Thermobalance (10 degrees C / min): 5% reduction (308 degrees C), 10% reduction (342 degrees C), 50% reduction (363 degrees C), 90% reduction (496 degrees C).

[0035] the bromination styrene oligomer manufactured in example 3 - example 4 example 1 or the example 2 -- the high-impact-polystyrene (Mitsubishi Chemical HT- omitted Following HIPS 88) 100 weight section -- receiving -- 20 weight sections -- antimony-trioxide 6.7 weight section combination was carried out, and injection molding was carried out using the twin screw extruder (ratio-of-length-to-diameter:25) with the melting temperature of 205-215 degrees C, and the die temperature of 45 degrees C.

[0036] Color difference measurement was carried out by the approach shown below using the obtained sample in an inflammable trial, workability (fluidity), shock resistance, the tension test and the bending test, and the list.

[0037] About the test piece created from the sample obtained by the <evaluation approach of inflammable trial> injection molding, the oxygen index measured UL combustion test based on the UL94V perpendicular flammability test method based on JIS-K -7201, respectively.

[0038] Based on JIS-K -6760, the melt flow rate (200 degree-Cx5kg) was measured using the pellet <evaluation approach of workability (fluidity)> Obtained.

[0039] The piece of a sample blank test obtained by <shock-proof> injection molding was produced, and Izod impact value was measured based on ASTM-D -256.

[0040] From the sample obtained by <tension test> injection molding, it pierced by the No. 3 dumbbell, the test piece was created, and it measured by part for 200mm/in tension rate.

[0041] The piece of a sample blank test obtained by <bending test> injection molding was produced, and it measured based on JIS-K -7203.

[0042] The 50mmx50mmx2mm test piece was produced from the sample obtained by <color difference measurement> injection molding, and the color difference with a standard white sheet was computed by the bottom type using the color difference meter.

[0043] W={ (100-L) 2+a2+b2 } 1 / 2 (L, a, and b express the measured value of a test piece among a formula) -- these results are united and shown in Table 1.

[0044]

[Table 1]

<配合組成(重量部)>	実施例3	実施例4	比較例1	参考
HIPS 実施例1の臭素化スチレンオルゴマー 実施例2の臭素化オルソオルゴマー 市販の臭素化オルソオルゴマー 三酸化アンチモン	100 20 -- -- 6.7	100 -- 20 -- 6.7	100 -- 20 -- 6.7	100 -- -- -- --
燃焼性試験 酸素指数 (O <sub>2</sub> %) <sup>1)</sup> UL-94 V燃焼性 <sup>2)</sup> 1/8インチ 1/16インチ	25.0	26.0	25.0	18.5 HB HB
加工性(流動性) MFR	1.6	2.0	8.2	7.6
耐衝撃性 (kgf·cm/cm <sup>2</sup> )	4.1	4.4	2.8	8.20
引張試験 降伏強さ (kgf·cm/cm <sup>2</sup> ) 破壊強さ (kgf·cm/cm <sup>2</sup> ) 伸び率 (%)	328 288 31	310 265 30	308 263 23	297 257 43.2
曲げ試験 曲げ弾性率 (kgf·cm/cm <sup>2</sup> ) 曲げ強さ (kgf·cm/cm <sup>2</sup> )	24400 491	23500 523	24500 445	22000 419
色差試験 (W値)	85.6	82.1	59.2	--

1) 酸素指数 : スガ試験機製 ON-1型  
2) UL 94 V燃焼性試験 : スガ試験機製 UL-94 V型

[0045] Using the bromination styrene oligomer (Ferro PAIRO check LM) of example of comparison 1 marketing, it blended with HIPS like the example 3 - the example 4, and the evaluation trial was carried out. A result is united and shown in Table 1. Moreover, various HIPS independent evaluation results were also shown in Table 1 as reference.

[Translation done.]